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Carbon Monoxide and Total Hydrocarbon Continuous Monitoring at Hazardous Waste Incineration Facilities

Entropy Environmentalists, Inc., Research Triangle Park, NC

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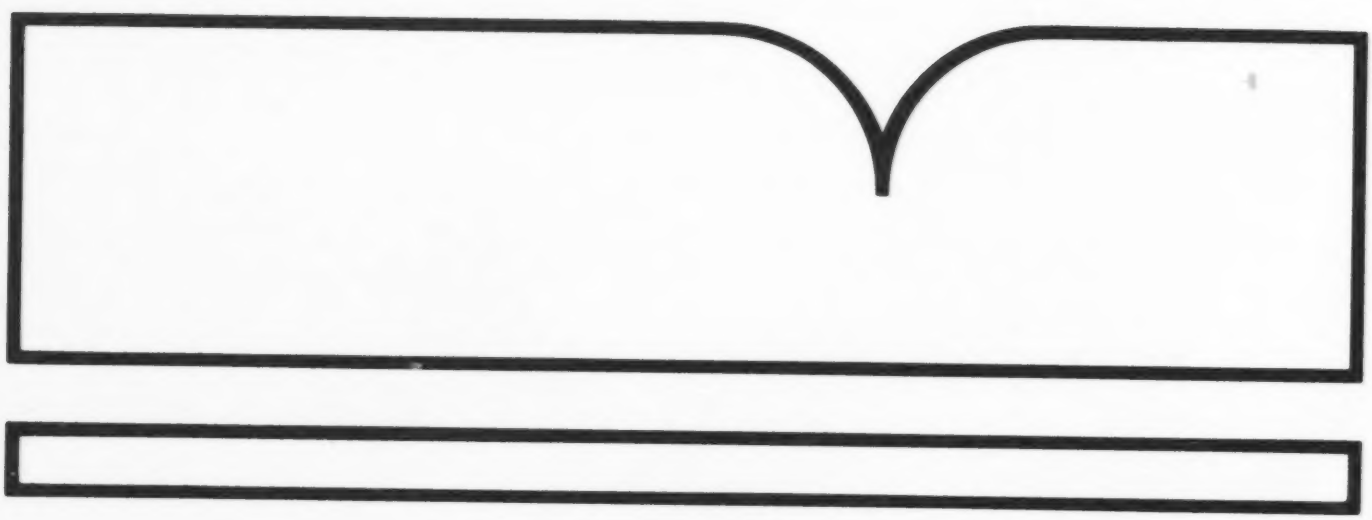

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16. ABSTRACT

Incineration is being viewed increasingly as the most practical, least harmful means of disposing of hazardous waste. The EPA has recently proposed continuous monitoring specifications and regulatory requirements which expand those established in 40 CFR Part 264, Subpart O, and the associated permit rules of 40 CFR Part 270. The regulations are intended to provide additional assurance that the operation of hazardous waste incineration facilities does not pose unacceptable risk to public health.

In support of these regulations, commercially-available carbon monoxide (CO) and total hydrocarbon (THC) continuous emissions monitors are being evaluated. Laboratory performance tests were conducted to determine characteristics such as calibration drift, linearity, and response time. Carbon dioxide interference in CO measurements and hydrocarbon instrument sensitivity to various hydrocarbons were also investigated. A field evaluation was conducted at a hazardous waste incinerator. The field test data provide information on individual analyzer operation and comparisons of measured CO and THC emissions. This paper discusses the test results, sample conditioning systems and monitors, and areas for further study.

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CARBON MONOXIDE AND TOTAL HYDROCARBON CONTINUOUS MONITORING AT HAZARDOUS WASTE INCINERATION FACILITIES

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Incineration is being viewed increasingly as the most practical, least harmful means of disposing of hazardous waste. The EPA has recently proposed continuous monitoring specifications and regulatory requirements which expand those established in 40 CFR Part 264, Subpart O, and the associated permit rules of 40 CFR Part 270. The regulations are intended to provide additional assurance that the operation of hazardous waste incineration facilities does not pose unacceptable risk to public health.

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Introduction

The U.S. Environmental Protection Agency (EPA) is in the process of proposing amendments to rules on hazardous waste incineration, under Subpart O of 40 CFR Part 264. The EPA is concerned that the existing standards may not control products of incomplete combustion (PIC's) adequately. In support of these proposed amendments, the EPA's Office of Solid Waste (OSW) and Atmospheric Research and Exposure Assessment Laboratory (AREAL) have sponsored several studies to document emissions from hazardous waste incineration (HWI) facilities and investigate the methodologies and instrumentation available to measure these emissions. Entropy Environmentalists, Inc. was contracted by the Quality Assurance Division of AREAL to evaluate commercially-available carbon monoxide (CO) and total hydrocarbon (THC) instruments.

This evaluation was conducted to determine field performance characteristics of CO and THC continuous emission monitors. Laboratory and field studies were performed to determine specific operating characteristics of the monitors and their reliability under continuous use.

Arrangements were made with monitor vendors for the loan of instruments to the EPA for evaluation. Several hydrocarbon monitor designs were considered initially, but instruments containing flame ionization detectors, or FID's, were determined to be most suited for this application. Although less sensitive to chlorinated and aromatic hydrocarbon species than Hall® and photoionization detectors, FID's are more rugged detectors, are linear over large concentration ranges and can provide continuous measurements over extended periods of time. Dual-range capability was the primary requirement for the inclusion of instruments in the CO monitor evaluation. Six hydrocarbon and three CO monitors were included at some point in the evaluation.

The laboratory and field evaluations were conducted during a five month period. General operation of the instruments was checked in the laboratory. Sample conditioning systems were designed to provide appropriate sample and calibration gas to each instrument. Arrangements were made to evaluate the field operation of these instruments at a hazardous waste incinerator. The host facility was a solid waste batch-fed incinerator and was chosen because of the occurrence of periodic CO spikes. The seven-week field evaluation was conducted to (1) define the necessary sample conditioning system characteristics, (2) determine instrument linearity, response time, and calibration drift for CO and THC monitors, (3) evaluate the relative responses of "hot" and "cold" THC monitoring systems (defined under monitoring system description), and (4) evaluate instrument performance over extended periods of field operation.

Monitoring System Description and Test Procedures

The monitoring system consisted of sample conditioning systems, analyzers, and a data acquisition system. Separate sampling systems were required to provide a hot, filtered sample for the hot FID's and a cooled, condensed, and filtered sample for the cold FID's, CO and O_2 monitors. (Hot systems must maintain the temperature of all components of the sampling system at a minimum of 150°C, as specified in EPA Test Method 25A. Cold FID

systems include some method of cooling and drying the sample to near ambient conditions.) Each instrument had specific requirements for sample gas pressure and flowrate. In the field, five instruments (two hot FID's, one cold FID, one CO, and one O_2) had internal pumps and required from 1 to 7 liters/minute of sample at ambient pressure. Four instruments (two CO, one O_2, and one cold FID) did not have pumps and required four different flowrates and sample pressures.

The two systems obtained sample gas from the same sampling probe. (See Figure 1.) The hot sample gas was transported through a heated line, a second heated filter, and into the heated analyzers. Both the Ratfisch 55 and JUM VE-7 analyzers contained a third heated filter immediately inside the analyzer cabinets.

The cold sample conditioning system used condensers to lower the sample temperature to approximately 5°C. Condensate was removed continuously to minimize condensate contact with the sample gas. A 2-micron coalescing filter downstream of the first condenser collected particulate matter not removed by the probe filter or with the condensate. Residual water vapor on the pressure side of the pump was captured in a post-pump condenser. The manifold used in the cold system allowed sample pressures and flowrates to be controlled individually for each analyzer. Both systems provided for calibration gas injection at the probe outlet and directly into the analyzers. The probe outlet injection point was upstream of the heated filter and allowed calibration gas to flow through the hot and cold systems simultaneously.

All cylinder gases used to evaluate the CO and O_2 monitors were EPA Protocol 1 gases. The propane and methane gases were "Acublend Master" gases with $\pm$ 2% concentration tolerance. A zero air generator was used to provide zero calibration gas and combustion air for the THC monitors. Comparisons with ultra-pure carrier grade air were performed to verify the quality of the generated zero air.

Table I presents a brief description of the hydrocarbon instruments included in the study. Each hydrocarbon instrument was equipped with an FID. Operation of the FID is based on a burner in which a small flame is sustained by carefully regulated flows of air and fuel (normally either pure hydrogen or a hydrogen/helium mixture). Sample gas enters the instruments at flows ranging from 2-7 liters/minute. In each instrument, a small slipstream is pushed through capillary tubing to the FID. The remaining sample is exhausted. The GC/FID instruments pass a portion of the sample gas through a chromatographic column to determine methane content. Precise regulation of the sample pressure is essential to accurate FID measurements. In most FID instruments the sample gas pressure is maintained by a backpressure regulator downstream of the FID. The JUM design is slightly different in that it uses a regulated supply of pressurized, hydrocarbon-free ambient air to provide the necessary back pressure to force the sample gas to the FID. The THC instruments which provided the majority of information during the field evaluation were the Ratfisch Models 55 and 102, the JUM VE-7 and the Beckman 400A.

All three CO instruments operated during both the laboratory and field evaluations. The ACS Models 3300 and 8000 are non-dispersive infrared (NDIR) analyzers which measure CO concentrations in the effluent continuously. These analyzers operate on the principle that CO has a unique

absorption spectrum in the infrared region. An infrared light beam emitted by the source passes through the measuring cell, which is filled with a continuously flowing gas sample. The light beam is partially absorbed or attenuated by the CO in the measuring cell before reaching the detector. The measurement ranges of the Models 3300 and 8000 were 0-500/0-2500, and 0-200/0-3000 ppm, respectively.

The TECO Model 48 employs gas filter correlation (GFC) to measure CO by infrared (IR) absorption. GFC employs a correlation wheel consisting of two hemispherical cells, one filled with CO and the other filled with nitrogen (N_2). Passing an IR beam through the CO gas cell in the correlation filter provides a reference signal that cannot be further attenuated by the CO in the gas sample. The N_2 cell is transparent to the IR radiation and therefore produces a measurement beam which can be absorbed by CO in the sample cell. The TECO analyzer was operated on a range of 0-2000 ppm CO (One of twenty selectable ranges). At the end of the test, the range was changed to 0-5000 ppm to provide a better indication of peak emission levels.

Infrared absorption is a non-linear measurement technique. To correct for this characteristic, instrument electronics convert the analyzer signal into a linear output. The ACS instruments utilized four potentiometers to make corrections to different portions of the measurement ranges. The calibration curve for the TECO is stored in the instrument's microcomputer memory and is used to linearize the instrument output over all ranges.

The computerized data acquisition system (DAS) developed by Entropy uses a hard disk and internal 12-bit analog-to-digital converter with a 16 channel multiplexer. Surge suppressors and a back-up power supply were provided to minimize data loss. In addition to providing an instantaneous display of analyzer responses, the DAS provided 1-minute, 15-minute, and 1-hour averaged data for each analyzer. The test results and calibrations were stored on the hard disk and printed on a printer. The emissions data files were transferred to a second computer for additional calculations, graphs and summary tables.

Results and Discussion

Carbon Monoxide Analyzer Performance

Performance testing was conducted during the laboratory evaluation to determine the calibration error, calibration drift, carbon dioxide interference, and response time of the CO analyzers.

Calibration error (linearity) tests were performed to provide an indication of accuracy over the entire measurement range. The four-point procedure used is a more rigorous check of the instrument linearity than the calibration error test described in the proposed CO performance specification.[1] This procedure requires that each instrument demonstrate linearity over the entire operating range, rather than at a single mid-point. Although the instruments were operated on the high ranges, the more stringent low-range criteria were used to assess the accuracy of the low-range responses, i.e., the percent of span result is calculated using 200 ppm as the span value for the two low range gases. The individual instrument ranges were used to calculate the two high level results. This

procedure was used to determine each instrument's ability to meet both the proposed low and high range specifications operating on a single range. This was necessary since the CO instruments evaluated either could not change ranges automatically or could not be calibrated in two ranges simultaneously. The data shown in Table II indicate that low level accuracy was not sacrificed while operating on a high range.

Seven-day drift tests were performed to determine the stability of the calibrations over time. The results were good for all three instruments. The average of zero, mid-range, and upscale results as a percent of span are shown in Table III. As with the calibration error calculations, zero and mid-range drift were calculated using 200 ppm CO as the span value. The instrument operating ranges of 2000 ppm for the TECO 48, 2500 ppm for the ACS 3300, and 3000 ppm for the ACS 8000, were used as the span value in the upscale drift determination.

Carbon dioxide (CO_2) interference checks were performed to quantify the effect, if any, of the presence of CO_2. Carbon dioxide alone and as a mixture with CO were examined. The cylinder gases used for the testing were 11% CO_2 in nitrogen, 100 ppm CO in air and 994 ppm CO in air. An oxygen monitor was zeroed with the CO_2 cylinder gas and calibrated to the air levels of the CO cylinders to allow accurate determination of the CO/CO_2 mixtures. The responses to gas injections of 50 ppm CO in the presence of 5.5% CO_2, and 500 ppm CO with 5.5% CO_2 ranged from -2 to +8 percent of the expected gas value. All three instruments showed little interference with injections of CO_2 alone.

The response time of each CO instrument was determined in the laboratory by alternating between zero and upscale (994 ppm) calibration gases. The time required to achieve 95% of the final stable response was 30 seconds for the ACS 3300, 45 seconds for the ACS 8000, and 60 seconds for the TECO 48. The criterion in the proposed performance specification is 1.5 minutes.

All CO instruments operated well throughout the field test. The TECO 48, which contained ambient temperature and sample pressure compensation capabilities, performed particularly well. The ACS 8000 drifted slightly around zero but maintained a very steady response to the upscale calibration gas. The ACS 3300 had the fastest response time, but drifted the most. The drift problems may be attributable to greater sensitivity to vibration and ambient temperature fluctuations.

CO emission patterns varied greatly during the test. A typical emission period is illustrated in Figure 2. In general, single spikes or periods of spikes occurred intermittently with periods of no measurable emissions. The spikes ranged from 200 ppm to above the instrument output limits. Spikes of 5000-7000 ppm were observed on the TECO 48 display several times during the test. No estimates of accuracy were made at these concentrations. The data illustrated in Figure 2 were obtained at the end of the test when the TECO 48 instrument range was changed to 0-5000 ppm CO to allow approximations of previously off-scale events. A calibration gas concentration of 1972 ppm CO was used during that period. A comparison of 15-minute averages obtained by the three analyzers throughout the test showed very good agreement, indicating that the differences in measurement technique and response time did not affect the quantification of the observed short spikes.

The oxygen concentration averaged between 12 and 14 percent, dry, during the field test, and dropped to 8-9 percent during upset periods. No corrected emissions data are presented in this document.

Total Hydrocarbon Analyzer Performance

Laboratory testing of the available THC monitors included checks of FID sensitivity, methane/propane comparisons, and instrument linearity. During the evaluation an external audit was conducted by Research Triangle Institute (RTI). The audit provided data on the sensitivity of different FID's to hydrocarbons known to be non-linear with respect to propane. These compounds, mainly aromatic and chlorinated species, are the primary constituents of concern in controlling products of incomplete combustion or PIC's. The results showed that the JUM, Beckman, and Ratfisch 552 were sensitive and similar in their responses. Chlorinated compounds, such as chlorobenzene and methylene chloride, were expected to have lower responses than the carbon number would indicate, but this was not observed. The instruments were calibrated before and after the audit with a 50 ppm propane-in-air cylinder gas. Since the audit gases were blended in nitrogen, no results were obtained using the CSI which requires that air be in the sample gas for combustion.

Methane and propane cylinder gases of the same concentrations (i.e., 10 and 50 ppm) were injected into the analyzers to determine response ratios and instrument linearity. Response to propane for the JUM, Beckman, and Ratfisch instruments was 2.4 to 2.6 times their response to methane. (The theoretical response to propane should be three times the response to methane.) The CSI response was approximately 1:1, demonstrating its ability to count molecules rather than carbon atoms. During instrument linearity determinations, none of the gas responses deviated from the expected value by more than 0.5% of the 100 ppm propane instrument span. A deviation of 5 percent of span is allowed in the proposed THC test method.[1]

The field evaluation was more complicated than expected. Providing a representative, appropriately conditioned sample at the correct pressure and flowrate to each analyzer was the greatest challenge of this project. Several problems encountered during the test could be attributed to actual analyzer design, but the majority were tied to the sample handling system. The high temperature, moisture and fine particulate levels at this facility prevented the planned seven weeks of continuous operation of the hot FID's, but provided valuable information on sample conditioning requirements.

The problems encountered with the hot FID measurements were similar for both the JUM and Ratfisch 55 analyzers. A fine particulate, possibly condensibles, accumulated in the heads of the sample pumps and at points downstream of the pumps, particularly the back-pressure regulators. The back-pressure gauges, requiring cooler operating conditions, were common points of condensate collection. The sample capillaries were also prone to periodic plugging.

As discussed in the system description, the CO and cold FID measurement system removed the water and condensible material from the sample gas. Cooling the sample simplifies the measurement process but could result in the loss of low boiling point and water soluble hydrocarbons. If these

compounds are present in the effluent, a difference in hot and cold FID measurements would be expected.

Hydrocarbon emission patterns as measured by both hot and cold systems were similar to those observed for CO, with little to no measurable emissions between spikes. The THC peaks coincided with those measured for CO. Cold FID measurements ranged from 50-100% of the hot measurements, with the level of agreement decreasing as the effluent level increased. Figures 3 and 4 illustrate emissions measured during the field test. The data illustrated in Figure 4 were obtained at the end of the test when the instrument ranges were changed to 0-500 ppm THC as propane to allow approximations of previously off-scale events. A calibration gas concentration of 40 ppm propane was used during that period. Additional comparisons are discussed in the next section.

Sample Conditioning

The difficulties with particulate collecting downstream of the hot FID pumps, and the pump and regulator failures may be reduced or eliminated with the addition of an external, large capacity, heated sample pump followed by a heated fine particulate filter and an atmospheric vent. The external filter temperature should be maintained between 150°C and the analyzer temperature so that the analyzer is never the cold spot in the system. Also, placing the filter on the positive pressure side of the main pump should provide for the filtration of particulate matter that may be the result of condensation in the pump. The atmospheric vent is needed to allow the instruments to pull a sample at ambient pressure.

An additional problem may be the lack of uniformity in sample line heating. The sample line used during this project was measured to be 305°F at a point 6 feet into the line and 275°F at the line outlet. The presence of relatively cool spots in the system may affect the hot THC measurements and any hot/cold THC comparisons.

The configuration of the cold FID sample conditioning system is comparatively straightforward. Two important factors are matching the heat transfer capability of the condenser to the effluent conditions and providing a means of continuously draining the condensate to minimize contact with the sample gas.

Hot vs. Cold FID Measurements

Data from this study indicate that all measurable increases in hot FID measurements were accompanied by increases in the cold measurements. In general, the hot and cold concentrations were comparable at levels below 20 ppm; the cold measurements were 50-70% of the hot values during high concentration spikes. This suggests a change in hydrocarbon species as concentrations increase. The cold systems may, nonetheless, serve as adequate, though less sensitive, indicators of upset conditions, since THC spikes were detected simultaneously by both systems. This is shown in Figure 5, which includes cold and hot FID rolling hourly averages from a rather eventful period. The corresponding 1-minute averages for the hot FID during the same period are shown in Figure 6 to provide a reference for actual peak height and frequency.

CO as a Surrogate for THC Emissions

The adequacy of CO as a surrogate for hydrocarbon emissions in general, and PIC's in particular, has become an important question. In the EPA guidance on PIC controls, it is stated that good combustion efficiency, as indicated by low CO emissions, decreases the risk from PIC emissions.[1] The emissions data gathered during this project show that all THC excursions coincided with CO excursions. Therefore, the question the data from this project raise is not whether a relationship exists between CO and THC emissions, but what elevated CO levels indicate a process upset requiring a change in system operation.

Conclusions

The laboratory and field evaluations were conducted over a five-month period. During the seven-week field evaluation, information was gathered concerning the feasibility of acquiring continuous, accurate measurements of hazardous waste incinerator emissions. The following conclusions are based on observations made during the field evaluation.

- All CO instruments evaluated were able to meet the criteria outlined in the proposed performance specification for CO monitors at HWI's.
- Spikes in CO emissions were very short in duration (i.e., 3 - 4 minutes).
- Spikes in hydrocarbon emission levels occurred only during periods of upset CO conditions.
- "Cold" hydrocarbon measurements ranged from 50-100% of the "hot" hydrocarbon measurements. In general, the higher the emission level, the larger the difference.
- Cold hydrocarbon measurement systems operate reliably and are not affected by the problems currently preventing long-term hot system operation.

Disclaimer

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Reference

1. Guidance on PIC Controls for Hazardous Waste Incinerators, EPA Hazardous Waste Incineration Guidance Series, Volume V, Appendix A, April 1989.

TABLE I. HYDROCARBON INSTRUMENT DESCRIPTIONS

Instrument	Heated[1] (Temp)	Fuel	Combustion Air	Fuel/Air Regulators	Measurement Technique
Ratfiach 102	No	H_2	zero air	No	FID
Ratfiach 55	Yes (160°C)	H_2	zero air	Yes	FID
JUM VE-7	Yes (180°C)	H_2/He	--[2]	Yes[3]	FID
Beckman 400A	No	H_2/He	zero air	Yes	FID
Ratfiach 552	Yes (160°C)	H_2	zero air	Yes	GC/FID[4]
CSI[5]	No	H_2	--[2]	Yes[6]	GC/FID

[1] Indicates whether instrument is heated and to what temperature.
[2] Ambient air is pulled in and purified within the analyzer.
[3] These regulators are set in the factory and cannot be adjusted.
[4] Includes gas chromatographic column for methane separation.
[5] Similar to a flame photometric detector, the THC mode of this instrument provides a molecule count, rather than a carbon count (i.e., 10 ppm propane response = 10 ppm methane response).
[6] Combustion air and sample gas are combined upstream of the air regulator. Sample gas must contain sufficient air levels for FID combustion to be maintained.

TABLE II. CO CEMS CALIBRATION ERROR RESULTS

	ACS 3300 (0-2500ppm) 2/16/89	ACS 8000 (0-3000ppm) 2/15/89	TECO 48 (0-2000ppm) 4/3/89
Gas Value	100	100	100
Average Response	100	102	100
% Gas Value	0.0	2.0	-0.4
% Span	0.0	1.0	-0.2
Gas Value	199	199	199
Average Response	200	195	199
% Gas Value	0.5	-2.0	0.0
% Span	0.5	-2.0	0.0
Gas Value	994	994	994
Average Response	1025	984	992
% Gas Value	3.1	-1.0	-0.3
% Span	1.2	-0.3	-0.1
Gas Value	1972	1972	1972
Average Response	1905	1944	1991
% Gas Value	-3.4	-1.4	1.0
% Span	-2.7	-0.9	1.0

NOTE: The span value is defined as 200 ppm for the two low range gases and as the individual instrument measurement range for the two high range gases.

TABLE III. CALIBRATION DRIFT (% OF SPAN)

	Average Zero Drift	Average Mid-Range Drift	Average Upscale Drift	Performance Specification Limit
TECO 48	0.0	--*	-0.4	± 5%
ACS 3300	0.7	-1.6	0.8	± 5%
ACS 8000	0.0	-0.3	-0.4	± 5%

* The instrument panel display used in the drift test was later shown to be 10ppm lower than the signal output, therefore no meaningful drift value is available for the mid-range.

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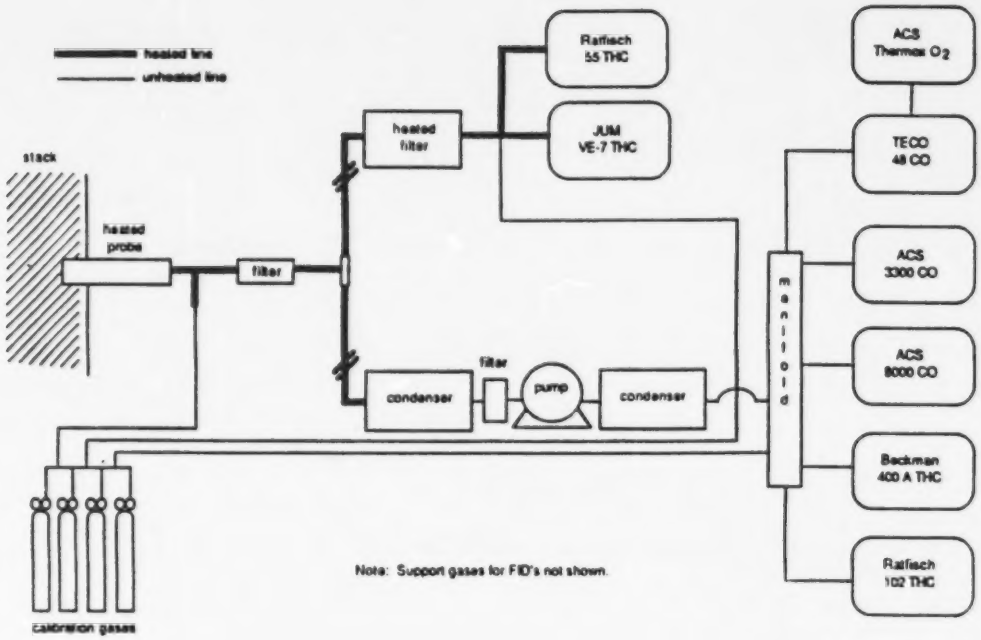

Figure 1. CO/THC sampling system configuration.

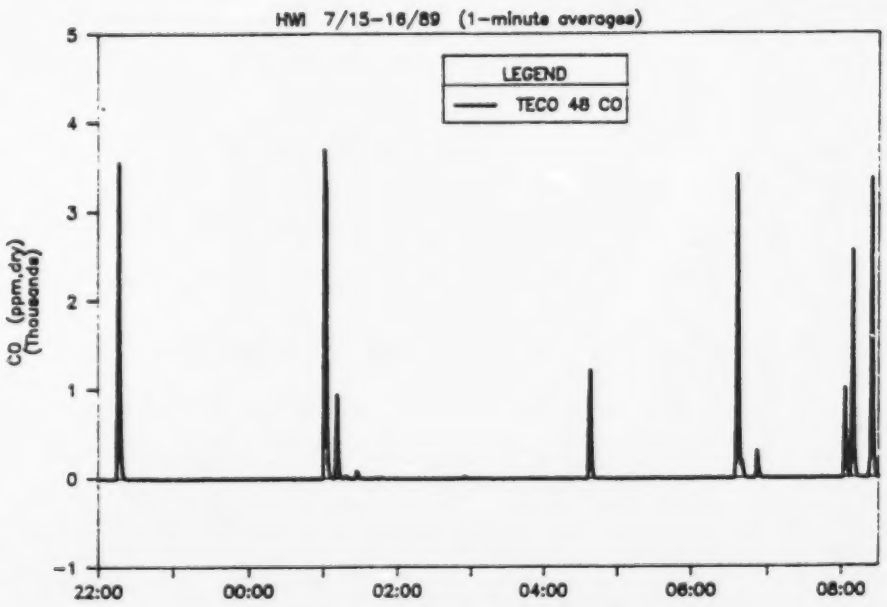

Figure 2. CO Emissions Data

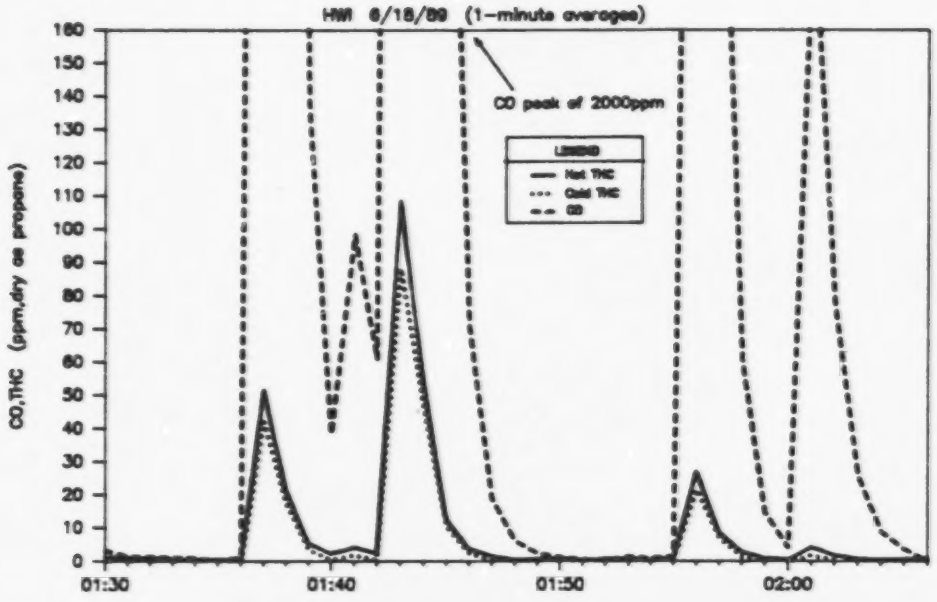

Figure 3. CO/THC Emissions Comparison

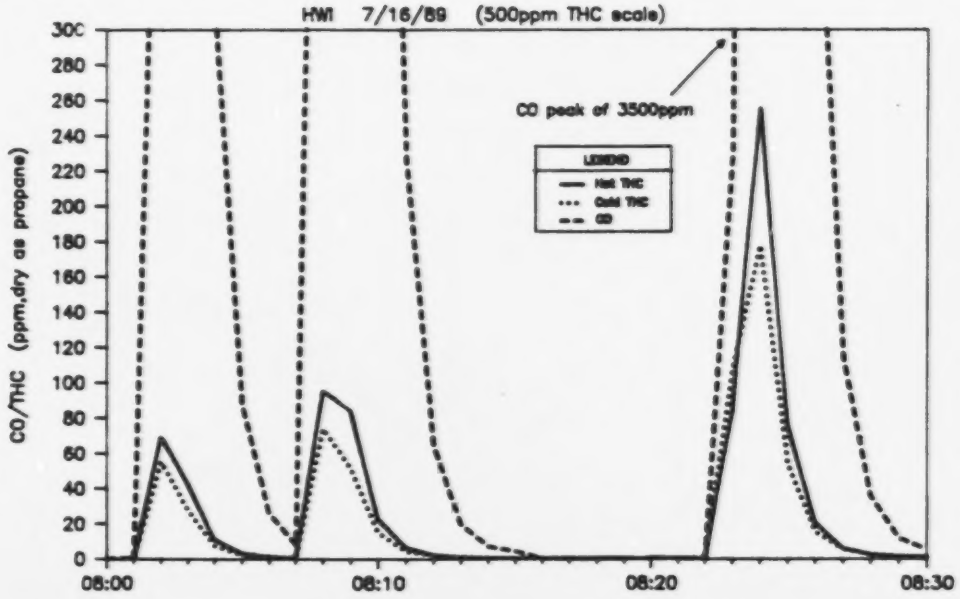

Figure 4. CO/THC Emissions Comparison

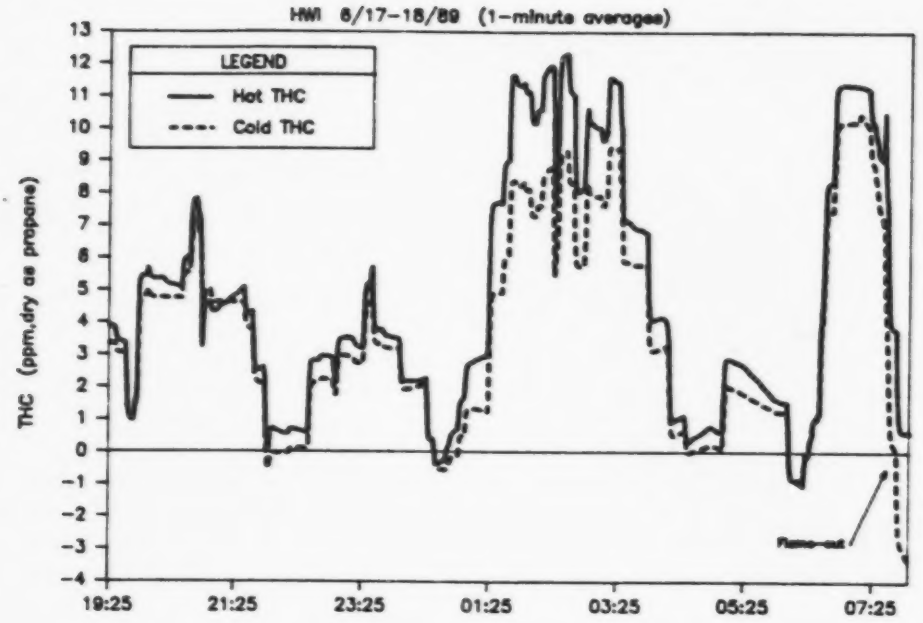

Figure 5. Rolling Hourly THC Averages

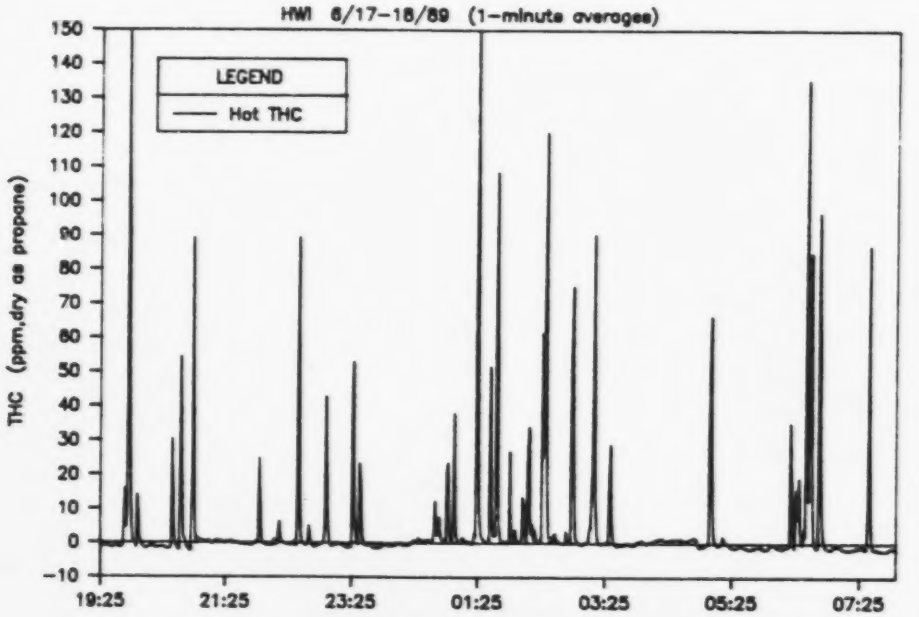

Figure 6. Hot THC Emissions Data